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Technical Report

MOLECULAR AND VALENCE STRUCTURES OF COMPLEXES OF
CYCLOOCTATETRAENE WITH IRON TRICARBONYL

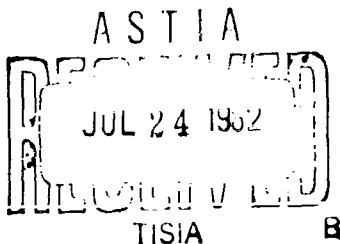
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This Technical Report is issued in connection with Contract No.
Nonr 1866(42), Task No. NR052-178 between the Office of Naval
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accordance with the Distribution List of 16 February 1962.

Submitted by:

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June 6, 1962



Molecular and Valence Structures of Complexes of
Cyclooctatetraene with Iron Tricarbonyl

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Abstract

Structure determinations by X-ray diffraction methods indicate that $\text{Fe}(\text{CO})_3$ units are bonded to a butadiene type of residue in $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ (I), and in $(\text{OC})_3\text{FeC}_8\text{H}_8\text{Fe}(\text{CO})_3$ (II), where the two $\text{Fe}(\text{CO})_3$ units are on opposite sides of the C_8H_8 ring. The dihedral C_8H_8 ring in (I) and the chair C_8H_8 ring in (II) are previously unknown and unsuspected geometries for cyclooctatetraene.

Crystals of (I) have symmetry $Pn\bar{m}$, within experimental error, with four molecules in a unit cell defined by the parameters $a = 6.54$, $b = 13.46$, $c = 11.50$ Å. Crystals of (II) are of symmetry $P2_1/n$, with four molecules in a unit cell which has parameters $a = 12.52$, $b = 13.38$, $c = 8.86$ and $\beta = 111^\circ$. Final values of $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ are 0.09 for (I) and 0.10 for (II) for all observed reflections.

The bonding of Fe to the butadiene-like residues is discussed.

Introduction. Cyclooctatetraene (COT) itself has been shown by X-ray methods^{1,2} and later by electron diffraction,³ to have a non-planar tub conformation in which the C=C distance of 1.33₄Å and the C-C distance of 1.46₂Å are close, respectively, to the values of 1.33₉Å for C₂H₄⁴ and 1.50Å for a single bond between carbon sp² hybrid orbitals.⁵ The geometry of COT is thus apparently dominated by the planar ethylene-like residues in the molecule and the tub-like conformation of COT is retained in the Ag(COT)⁺ complex.⁶ The failure of COT to show aromatic character receives its most natural rationalization from molecular orbital (MO) theory which yields, in the one electron MO approximation, two unpaired electrons if the molecule has planar D_{8h} symmetry or the non-planar crown D_{4d} symmetry. In either case one might then expect COT to accept electrons to become COT⁻ or COT⁻², recently prepared,^{7,8} or to undergo distortion from D_{8h} or D_{4d} to a lower symmetry so that the orbital degeneracy is removed and all electrons in neutral COT can be paired.

The preparation of (COT)Fe(CO)₃, (OC)₃Fe(COT)Fe(CO)₃ and of (COT)Fe₂(CO)₇ first by Manuel and Stone,⁹ and of one or two of these compounds almost simultaneously by five other research groups,^{10,11,12} was largely stimulated by an extension of ideas of transition metal-aromatic hydrocarbon bonding to seven and eight membered rings, a subject of considerable recent activity. The three classes of investigators who proposed structures, all

incorrectly, for the geometry of the COT ring in these complexes are those^{9,10,11} who prepared the compounds, those^{13,14,15} who could not await our promised⁹ X-ray diffraction results, and those¹⁶ (including ourselves) who did not publish. The observation^{9,10} of a single sharp proton resonance in the nuclear magnetic resonance spectrum and the shift of the C=C stretching frequency toward that in ferrocene apparently led to heavy favoritism for the suggestions^{9,10,13,14,15} of the planar COT ring in $(\text{COT})\text{Fe}(\text{CO})_3$, but two suggestions of the tub form occurred.^{11,17} The larger variety of suggestions, also incorrect, for the geometry of (COT) in $(\text{OC})_3\text{Fe}(\text{COT})\text{Fe}(\text{CO})_3$ are summarized in our preliminary communications.^{18,19}

Our X-ray diffraction studies of single crystals of $(\text{COT})\text{Fe}(\text{CO})_3$ and $(\text{OC})_3\text{Fe}(\text{COT})\text{Fe}(\text{CO})_3$, described below, show that the bonding of $\text{Fe}(\text{CO})_3$ to butadiene-like residues of the COT ring actually dominates the ring geometry. The dihedral form and large C-C-C bond angles of the COT ring in $(\text{COT})\text{Fe}(\text{CO})_3$, and the chair form of the oval shaped COT ring in $(\text{OC})_3\text{Fe}(\text{COT})\text{Fe}(\text{CO})_3$ are hitherto unknown geometries. Although these results add variety to the predictability of COT geometry in various situations, they also lead to the possibility of a general principle of bonding between $\text{Fe}(\text{CO})_3$ and a butadiene unit when such a unit is more readily available on energetic grounds than it is in ferrocene. We describe experimental results first for the $(\text{OC})_3\text{Fe}(\text{COT})\text{Fe}(\text{CO})_3$ crystals.

Structure Determinations. Yellow air-stable crystals of $(OC)_3Fe(COT)Fe(CO)_3$, obtained from dichloromethane-pentane solution, were chosen. Maximum cross-sectional dimensions of 0.14 and 0.12 mm were sufficiently comparable with $(4\mu)^{-1} = 0.11$ mm, where μ is the linear absorption coefficient for MoK α radiation, to allow us to neglect absorption corrections. Reciprocal lattice symmetry of C_{2h} , and extinctions of $0k0$ when k is odd and of $h0l$ when $h+l$ is odd lead to the monoclinic space group $P2_1/n$. Cell parameters of $a = 12.529 \pm 0.006$, $b = 13.377 \pm 0.013$, $c = 8.868 \pm 0.008$ Å and $\beta = 111.0^\circ \pm 0.2$ were obtained from $h0l$ and $hk0$ photographs upon which powder patterns of NaCl were superimposed. Assumption of four molecules in the unit cell leads to $\rho = 1.84$ gm cm $^{-3}$ in good agreement with the measured density of $\rho = 1.85$ gm cm $^{-3}$. For the visual intensity estimates, obtained with a standard scale of timed exposures of a reflection from the same crystal, the levels hkL for $0 \leq L \leq 3$; hKl for $0 \leq K \leq 4$; Hkl for $0 \leq H \leq 4$; hhl ; hkh ; $h+1, k, h$; $h+2, k, h$; $2h, k, h$; $hk\bar{h}$; $h, k, \bar{h}+1$; $hk, \bar{h}+2$; $h, k, 2\bar{h}$; $3h, 2h, l$; $h, 6h, l$; $2\bar{h}, k, h$ and $h, 2h, l$ were photographed with the use of the precession method and MoK α radiation. Intensities were corrected to F_{hkl}^2 , correlated, and scaled statistically prior to computation of the three dimensional Patterson function which was sharpened with the aid of the gradient function^{20,21} so that the average of the innermost reflections was about twice that of the outer reflections. The increased resolution of the gradient modification of the Patterson function greatly facilitated the analysis of the vector map.

The structure of $(OC)_3Fe(COT)Fe(CO)_3$ was solved by location of the Fe...Fe vectors, and the subsequent computation of a three-dimensional electron density map, $\rho(x,y,z)$, from which the Fe's were subtracted. After the usual intermediate stages which should have been straightforward but almost never are, except in retrospect, the entire molecule was located, and then refined by three dimensional least squares procedures. Three dimensional least squares refinements proceeded from three cycles with Fe atoms only in which $R(F^2) = \sum |F_o|^2 - |F_c|^2 / \sum |F_o|^2$ for all 977 observed reflections reduced to 0.76, through isotropic refinement in which all atoms except H yielded for the 334 largest reflections a decrease from $R(F^2) = 0.40$ to 0.32, a test including all observed reflections in which the slightly non-linear Fe-C-O groups were forced into linearity and refined to $R(F^2) = 0.31$ while the O displaced about 0.05Å to make Fe-C-O non-linear again, five more cycles in which individual isotropic temperature factors on all atoms were varied to yield $R(F^2) = .22$, two cycles in which Fe atoms only were allowed to have anisotropic temperature factors yielding $R(F^2) = 0.18$, to a final least squares cycle in which H atoms were added assuming trigonal hybrids at C and in which all position parameters except those of H were varied. Final values of $R(F^2) = 0.17$ and R (Table 1) = 0.10 were achieved. In all of these refinements our usual set of weights appropriate to visual estimates were employed. Although some definite indications of the H atoms were present in a three-dimensional electron density map from which Fe, C, and O were

subtracted, these H atom positions did not seem reliable enough to form a basis for refinement.

Reddish brown plate-like crystals of $(\text{COT})\text{Fe}(\text{CO})_3$, obtained by sublimation, were mounted inside a thin Mylar envelope inside of which a few additional crystals were held in order to maintain an equilibrium atmosphere of COT. Deterioration of the crystal under study was further retarded by passing a near 0°C stream of dry N_2 around the envelope in the usual way.²² Crystals were 0.21 and 0.30 mm in maximum diameter, comparable with $(4\mu)^{-1} = 0.34$ mm, and hence absorption corrections were omitted. The reciprocal lattice symmetry is D_{2h} , and the absence of $Ok\bar{l}$ when $k+l$ is odd and of $h0\bar{l}$ when h is odd suggest either Pnam or $\text{Pna}2_1$, as the space group possibilities. Unit cell dimensions, calibrated with NaCl powder patterns, are $a = 6.544 \pm 0.008$, 13.455 ± 0.023 and 11.506 ± 0.021 Å. The assumption of four molecules in the unit cell gives a calculated density of 1.60 gm cm^{-3} (observed value 1.57 gm cm^{-3}). Levels which were photographed, all with $\text{MoK}\alpha$ radiation and the precession method, are $hK\bar{l}$ for $0 \leq K \leq 5$; $Hk\bar{l}$ for $0 \leq H \leq 2$; hkL for $0 \leq L \leq 5$; $h, 2h, \bar{l}$; $h, 2h-1, \bar{l}$; $h, 2h-2, \bar{l}$; hkk ; $h, k, k+1$, and hhl . Corrections, correlations, and scaling on the observed data and the subsequent computation of a three-dimensional Patterson function, as described above, were also carried out.

The structure of $(\text{COT})\text{Fe}(\text{CO})_3$ was solved from the Patterson function and successive electron density maps. The Fe atoms were located in the mirror plane of the space group Pnam , and hence the assumption (later proved correct within standard deviations) was made that this space group mirror plane bisected the $\text{Fe}(\text{CO})_3$ unit and the COT ring. If the asymmetric unit of the unit cell contains only one Fe, at $x = 0.25$, $y = 0.06$, $z = 0.25$, calculated from the Patterson map, there is, as well as the space group mirror plane at $z = 0.25$, a pseudo mirror plane at $x = 0.25$, so a three dimensional electron density map calculated from the Fe phases (signs) showed the molecule superimposed upon its pseudo-mirror image. A CO group in a chemically reasonable and crystallographically general position was chosen, and, after least squares refinement of the y coordinate and the isotropic temperature factor of Fe, a second three dimensional map was computed from which an $\text{Fe}(\text{CO})_3$ group of reasonable geometry was chosen. Also six of the C atoms of the COT ring were found at geometrical positions corresponding to the Fe-butadiene residue, and its reasonable bonding to two other C atoms of the COT ring. Two of the C atoms, those at the apex of the dihedral form of the ring, were not unambiguously indicated and were therefore omitted at this stage. After least squares refinement of the partial structure to $R(F^2) = 0.40$, a three-dimensional electron density map was computed from which these last two C atoms were easily

located, and from which the pseudo symmetry was now absent. Seven cycles of least squares refinement led to a decrease of $R(F^2)$ from 0.33 to 0.16 for the 172 largest observed reflections, three cycles in which all 856 observed reflections were included reduced $R(F^2)$ from 0.24 to 0.19 and, finally, H atoms were introduced at chemically reasonable positions and all other coordinates and anisotropic temperature factors were varied (where allowed by the space group symmetry) in four cycles in which $R(F^2)$ became 0.16. The more usual R values are shown in Table 1. Because of this very satisfactory agreement, no refinements were carried out in the space group $Pna2_1$. Since any molecular distortions to lower symmetry would certainly have to be small, comparable with the standard deviations tabulated below, the molecular geometry is well established with only a probable resolution of the space group ambiguity.

Results and discussion. Drawings of the two molecules are shown in Figures 1, 2 and 3, as obtained from the final coordinates of Tables 2 and 4. Intramolecular bond distances and standard deviations are shown in Tables 3 and 5, and the experimental data are summarized in a compressed form in Tables 6 and 7. Standard deviations of coordinates, distances and angles were computed from the full matrix, including off-diagonal terms. Within the standard deviations the molecule of $(OC)_3Fe(COT)Fe(CO)_3$ has a center of symmetry which, however, is not utilized by the space group. Also within the standard deviations the

$(H_4C_4)Fe(CO)_3$ butadiene-type of residues have the same geometry in both molecules. The FeCO groups are non-linear in both compounds, the largest deviation from linearity being $7.1^\circ \pm 1.5^\circ$ for FeC_5O_5 in $(COT)Fe(CO)_3$. None of the remaining deviations is significant statistically, and all are assumed to be associated with intermolecular forces in the molecular packing or with errors in the final parameters of the structures. The average CO distances of 1.15Å and 1.13Å are not significantly different from one another, or from the distance of 1.13Å in CO itself. If one chooses the digonal radius of 0.73Å for C and omits the electronegativity correction of $-0.08 (2.5-1.8) = -0.056$ Å, the single bond Fe-C distance is $1.24\text{Å} + 0.73\text{Å} = 1.97\text{Å}$. The Fe-C (carbonyl) distances are about 0.17Å shorter than this single bond distance, a shortening which is consistent with some π donation from bonding CO to vacant d on Fe, some back donation from filled d on Fe to vacant antibonding π on CO (Figure 4), and perhaps some further shortening because C has only two neighbors.²⁸ These effects are not separable, but since the back donation would clearly reduce the formal negative charge on Fe and thus stabilize the FeCO bonding,²⁹ it is assumed that this mechanism is responsible for most of the Fe-C bond contraction. Such bond shortening is in accord³⁰ with the observed low C-O stretching frequency (2058, 1992 cm^{-1}) when compared with that of free C-O (2170 cm^{-1}).

The two new geometrical COT configurations^{18,19} seem to us to be forced on the ring by the domination of the Fe-butadiene-like residues in the structures as discussed below. Overlap integrals between SCF³¹ carbon π orbitals are summarized in Tables 3 and 5. The C_1-C_2 types of overlap integral (0.16) are similar in both compounds, and are less than that in butadiene because the C_1 $2p_\pi$ orbitals are directed out of the C_4 plane towards Fe. The near planarity of the C_4 unit bonded to Fe is responsible for the large C_1-C_2'' overlap (0.32) in both compounds; since the C_1-C_2 overlap is only 0.16 the C_2-C_2'' distance of 1.40 and 1.42 Å (Tables 3 and 5) is less than that in free butadiene and the C_1-C_2 and C_2-C_2'' distances are more nearly equal. The electronic near-isolation of the two butadiene-types of residues in $(OC)_3Fe(COT)Fe(CO)_3$, as indicated by the C_1-C_1' overlap integral of only 0.04 and by the near single bond distance of 1.49 Å (average) close to that (1.50 Å) expected,⁵ is the most striking feature of the COT ring in this compound. In $(COT)Fe(CO)_3$ a larger π orbital interaction between the butadiene-like residue and the remainder of the ring is suggested by the corresponding overlap integral of 0.25 between C_1 and C_3 ; indeed the unbound remainder of the ring is not only very nearly planar, as required for maximum overlap in the free half of the ring where an uncoordinated butadiene unit is formed, but the bond angles, with only two exceptions out of eight, are within about 3° of the

very large angle of 135° expected for a completely planar octagon (Figure 5).

This demonstration that the strain to make the COT ring planar or nearly so has been overcome in COT Fe(CO)_3 may have some relation to the recent proposal^{7,8} that the $(\text{COT})^-$ ion may be planar, and to the equal bond distances predicted^{32,33} for $(\text{COT})^{-2}$ ion which shows rapid electron exchange⁸ with $(\text{COT})^-$ ion. The interpretation³⁴ of experimental evidence on the hyperfine structure of the electron spin resonance of $(\text{COT})^-$ seems to be ambiguous with respect to the question of planarity of the ion, and hence the questions of small distortions into non-planarity, possibly into the crown form, have not been settled either for $(\text{COT})^-$ or for $(\text{COT})^{-2}$. An X-ray diffraction investigation of $\text{K}_2(\text{COT})$ ⁷ may be of value. Moreover, further theoretical studies of Jahn-Teller distortions in $(\text{COT})^-$ and of non-planar distortions in both ions need to be carried out in order to show whether the addition of an extra electron ("the one over the eight") to an antibonding level in non-planar COT is sufficiently stabilized by planarity or near planarity of the $(\text{COT})^-$ ion.

Two different proton nuclear magnetic resonance signals in a 1:1 ratio have been observed¹⁷ in a solution of $(\text{OC})_3\text{Fe}(\text{COT})\text{Fe}(\text{CO})_3$ in DCCl_3 . Comparisons of the infrared spectra of the two COT iron-tricarbonyl complexes in the solid state and in solution in bromoform indicate that their respective molecular

geometries are the same in the solid and solution states. Thus the single sharp proton resonance in the nuclear magnetic resonance spectrum of a solution of $(\text{COT})\text{Fe}(\text{CO})_3$ in CS_2 is apparently not due to negligible chemical shifts between the different protons, or to the presence of a different geometry, including the planar form of COT, in solution from that in the solid. Any proposed exchange mechanism accounting for this single proton resonance must explain why the protons in $(\text{COT})\text{Fe}(\text{CO})_3$ exchange, while those in $(\text{OC})_3\text{Fe}(\text{COT})\text{Fe}(\text{CO})_3$ do not. A dynamical effect amounting to permutation of the C atoms of the ring relative to the $\text{Fe}(\text{CO})_3$ group does, however, satisfy the experimental observations. There is continuous π - π overlap of 0.16 or more around the dihedral form of the ring, while in the chair form the C_1 - C_1' π - π overlap is only 0.04. Consequently in the chair form rotation in an analogous fashion is seriously inhibited, and two different types of protons are observed. The effect of ring substitution in the dihedral form is shown in the broadened resonance obtained³⁵ for the COT protons in the nuclear magnetic resonance spectrum of $(\text{C}_6\text{H}_5\text{-C}_8\text{H}_7)\text{Fe}(\text{CO})_3$. A temperature dependence study of the resonance spectrum of $(\text{COT})\text{Fe}(\text{CO})_3$ may clarify the above situation.

In the orbital overlap investigation of the iron-butadiene residue unit SCF orbitals³⁶ were used for Fe 1s through 4s, Slater orbitals³⁷ for Fe 4p and carbon 1s and 2s, and SCF orbitals³¹ for the carbon 2p. The Fe orbitals were referred to

cartesian coordinates about the "best" three-fold axis defined by the three carbonyl groups; their overlaps with the various carbon orbitals are presented in Table 8.

Trigonal bipyramidal hybridisation of the Fe is excluded by the absence of C-Fe-C angles near 120° ; square pyramidal coordination not only takes no account of the shorter Fe-C₂ distance (2.05Å) over the Fe-C₁ (2.18Å) distance, when geometrical considerations would prefer Fe bonded more to C₁ than to C₂ since C₁-Fe-C₁["] is $88.5^\circ \pm 0.5$ while C₂-Fe-C₂["] is $40.7^\circ \pm 0.6$, but also is refuted by the $\langle d^2sp^3 | C_2 + C_2'' \rangle$ σ bond value of 0.22, where no appreciable overlap would be expected.

Two models of Fe-COT bonding which give diamagnetic structures are left. The octahedral model has as ligands the three carbonyl groups, the C₁ and C₁["] carbons, and the C₂ + C₂["] double bond; orbital overlaps for σ type bonds with the appropriate d^2sp^3 Fe orbitals are 0.50, 0.15 and 0.22 respectively. Table 8 shows that appreciable π bonding between the d^2sp^3 orbitals and the 2p orbitals on the ligands is possible. Overlap of the t_{2g} 3d orbitals, not involved in the d^2sp^3 hybridisation, with the antibonding orbital at C₂ and C₂["], has a value of 0.08, and could account for possible back donation to this section of the butadiene residue. The maximum back donation overlap of these t_{2g} 3d orbitals with the antibonding orbitals of a carbonyl group is estimated at 0.17.

A model in which Fe is treated as seven-coordinated splits the double bond contribution of C_2+C_2'' in the octahedral model into two separate interactions by hybridizing the t_{2g} orbitals with the appropriate d^2sp^3 orbital to form sigma type bonds to each C_2 . Due to the orthogonality restriction between the resulting hybrids the individual $\langle d^5sp^3 | C_2 \rangle$ have maximum values of 0.17, to be compared with 0.18 for $\langle d^2sp^3 | C_2 \rangle$. The best choice of orbital coefficients in the new d^5sp^3 orbitals ϕ and ϕ'' ,

$$\phi = .689 (d^2sp^3)_z - .611 3d_{y_h z_h} + .389 3d_{x_h z_h} - .028 3d_{x_h y_h}$$

$$\phi'' = .689 (d^2sp^3)_z - .611 3d_{x_h z_h} + .389 3d_{y_h z_h} - .028 3d_{x_h y_h}$$

together with the interorbital angle of 40° , close to that of C_2FeC_2'' , brings out the importance of π type bonding over σ type in the Fe-butadiene unit at these interatomic distances. This seven-bond model is supported by the approximately equal C_1-C_2 and C_2-C_2'' distances in the coordinated C_4 group. The short Fe- C_2 distance of 2.06 supports the octahedral model via back donation. It can only be concluded that the "true" picture is probably somewhere between these two extremes, though possibly nearer the latter.

Geometries close to those of the butadiene iron tricarbonyl residues reported here have now been observed, by X-ray diffraction studies, in several analogous compounds (Fig. 6). The

extreme dislocation of the dihedral form of COT, and the electronic isolation in each half of the chair form, produced by the $\text{Fe}(\text{CO})_3$ group, are indications of the great strength of the Fe-C interactions. Additional evidence for both the strength of Fe-C bonds and the excellence with which the butadiene residue meets the spatial requirements of Fe is found in the inducement of butadiene residues by $\text{Fe}(\text{CO})_5$ and related carbonyls in 1:4 pentadiene,³⁸ 1:4 dihydromesitylene,³⁹ and vinylcycloheptatriene,⁴⁰ all of which possess unconjugated double bonds.

A butadiene residue unit is apparently preferred when an $\text{Fe}(\text{CO})_3$ group combines with an organic molecule in which no ferrocene fragment is available; many compounds^{38,39,40,41,42,43,44,45} containing $\text{Fe}(\text{CO})_3$ groups probably contain such a unit. Since no $\text{C}_6\text{H}_6\text{Fe}(\text{CO})_3$ complex is known, unsubstituted benzene appears to be a sufficiently stable system to resist the temptation to deform, but meta and para divinylbenzene both form complexes³⁹ with $\text{Fe}_3(\text{CO})_{12}$. Here a vinyl double bond is used as one half of the butadiene residue and a double bond of the benzene ring can be used for the other half, since in the 10π electron system of divinyl benzene the stability of the benzene π electron system has been disrupted by the additional electron delocalisation afforded by the vinyl groups. In 1-phenyl butadiene no disturbance of the benzene ring is necessary to form a butadiene residue, and hence a normal, substituted butadiene complex is formed.³⁹

The butadiene residue unit, purely because it has four available π electrons in a suitable spatial arrangement for appreciable overlap with the Fe orbitals, is a highly characteristic ligand of the $\text{Fe}(\text{CO})_3$ group. In the formation of a butadiene residue, only the organic π electron density is important; in this respect the apparently anomalous complexes of 2,2,1 bicycloheptadiene⁴⁵ and 1,5 cyclooctadiene³⁸ are analogous to the more normal complexes although they differ in their σ bond frameworks. Complexes, $\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$, of the three isomers of C_8H_{10} , 1,3,5-octatriene, 1,3,6-cyclooctatriene and (4,2,0) bicycloocta 2,4 diene, all of which possess butadiene-like π electron densities, but differ in the rest of the molecule, are well characterised.⁴⁵

Acknowledgement

We wish to thank the Office of Naval Research for financial support, and to thank Dr. T. A. Manuel and Dr. F. G. A. Stone for the samples used in this study. We acknowledge the use of the Least Squares Refinement Program of W. R. Busing and H. A. Levy, the Fourier Series Program MLFR1 by W. G. Sly and D. P. Shoemaker, and the Diatomic Molecular Integral Program by A. C. Switendick and F. J. Corbató in this study. We wish to record appreciation to Russell M. Pitzer for helpful discussions concerning the orbital calculations.

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Table 1. Summary of Agreement, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

A. $(OC)_3Fe(COT)Fe(CO)_3$, 977 F_o 's.

R as a function of $\sin \theta$			
hkl for	R	Range of $\sin \theta$	R
all observed	0.11	0.00 - 0.10	0.11
h even	.11	0.10 - 0.15	.10
k even	.11	0.15 - 0.18	.10
l even	.11	0.18 - 0.22	.09
h+k even	.12	0.22 - 0.26	.08
h+l even	.11	0.26 - 0.30	.10
k+l even	.10	0.30 - 0.35	.12
h+k+l even	.11	0.35 - 0.40	.15
hko	.10	0.40 - 0.45	.22
hol	.13	0.45 - 1.00	.26
okl	.14		

B. $(COT)Fe(CO)_3$, 856 F_o 's

R as a function of $\sin \theta$			
hkl for	R	Range of $\sin \theta$	R
all observed	0.09	0.00 - 0.10	.18
h even	.09	0.10 - 0.20	.09
k even	.10	0.20 - 0.30	.06
l even	.10	0.30 - 0.35	.07
h+k even	.09	0.35 - 0.40	.09
h+l even	.09	0.40 - 0.45	.12
k+l even	.08	0.45 - 0.50	.17
h+k+l even	.10	0.50 - 0.60	.14
hko	.08		
hol	.08		
okl	.08		

Table 2. Atomic Parameters and Standard Deviations
for $(OC)_3Fe(COT)Fe(CO)_3$

Atom	x_1	y_1	z_1	B_1^a	x_1	y_1	z_1
Fe'	0.2235	0.3056	0.7034	2.54	0.0003	0.0003	0.0004
Fe	.2655	.4438	.2741	2.11	.0004	.0003	.0004
C ₁	.343	.327	.442	2.93	.002	.002	.003
C ₂	.248	.291	.309	4.45	.002	.002	.003
C ₂ '	.142	.339	.263	4.00	.002	.002	.003
C ₁ '	.129	.419	.357	3.68	.002	.002	.003
C ₁ ''	.143	.422	.533	4.27	.003	.002	.003
C ₂ ''	.234	.456	.675	3.20	.002	.002	.003
C ₂ '	.342	.411	.712	3.83	.002	.002	.003
C ₁ '	.363	.328	.617	3.29	.002	.002	.003
C ₅	.330	.540	.415	3.13	.002	.002	.003
O ₅	.376	.602	.502	5.61	.002	.002	.002
C ₆	.371	.425	.188	4.08	.003	.002	.003
O ₆	.442	.416	.134	6.37	.002	.002	.003
C ₆ '	.181	.513	.104	3.43	.002	.002	.003
O ₆ '	.126	.562	-.003	5.48	.002	.002	.002
C ₃	.158	.211	.570	3.80	.002	.002	.003
O ₃	.118	.144	.476	4.95	.002	.002	.002
C ₃ ''	.115	.319	.793	3.14	.002	.002	.003
O ₃ ''	.044	.326	.842	5.17	.002	.002	.002
C ₃ '	.318	.237	.868	4.14	.002	.002	.003
O ₃ '	.371	.184	.966	6.58	.002	.002	.003

^a The B_1 are isotropic temperature parameters in \AA^2 . Anisotropic components for the two Fe atoms are $(\beta_1)_{11} = 0.0031$, $(\beta_1)_{22} = 0.0033$, $(\beta_1)_{33} = 0.0129$, $(\beta_1)_{12} = 0.0003$, $\beta_{13} = 0.0043$, $(\beta_1)_{23} = 0.0009$, $(\beta_2)_{11} = 0.0065$, $(\beta_2)_{22} = 0.0026$, $(\beta_2)_{33} = 0.0131$, $(\beta_2)_{12} = -0.0001$, $(\beta_2)_{13} = 0.0061$ and $\beta_{23} = -0.0001$ where the isotropic and anisotropic temperature factors are $\exp(-B_1 \lambda^{-2} \sin^2 \theta)$ and $\exp[-(\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + \beta_{12} hk + \beta_{13} hl + \beta_{23} kl)]$ respectively.

Table 3. Distances (in Å), Angles ($^{\circ}$), Standard Deviations (σ) in $(OC)_3FeC_8H_8Fe(CO)_3$.

FeC(COT)	Dist.	σ	$\angle C_1C_2C_2'$	Angle	σ
Fe'-C ₂ '	2.03	0.03	C ₂ 'C ₂ 'C ₁ '	123	2
Fe'-C ₂ '	2.04	0.02	C ₁ 'C ₂ 'C ₂ '	118	2
Fe-C ₂ '	2.06	0.03	C ₁ 'C ₂ 'C ₂ '	121	3
Fe-C ₂	2.09	0.03	C ₂ 'C ₂ 'C ₁ '	119	2
Av(FeC ₂)	2.06		Av $\angle C_1C_1C_2$	120	
Fe ₁ -C ₁ '	2.15	0.03	C ₂ 'C ₁ 'C ₁	128	2
Fe ₁ -C ₁ '	2.17	0.03	C ₁ 'C ₁ 'C ₂	130	2
Fe-C ₁	2.14	0.02	C ₂ 'C ₁ 'C ₁ '	129	3
Fe-C ₁ '	2.12	0.03	C ₁ 'C ₁ 'C ₂ '	133	3
Av FeC ₁	2.14		Av	130	
C(COT)C(COT)			$\angle FeCO$		
C ₂ '-C ₂ '	1.40	0.04	Fe ₁ C ₆ O ₆	173	3
C ₂ '-C ₂	1.39	0.04	Fe ₁ C ₆ 'O ₆ '	177	2
Av C ₂ C ₂	1.40		Fe ₁ C ₅ O ₅	176	2
C ₁ -C ₂ '	1.48	0.04	FeC ₆ 'O ₆ '	177	3
C ₁ '-C ₂ '	1.44	0.03	FeC ₆ O ₆	178	3
C ₁ -C ₂	1.43	0.03	Fe C ₅ O ₅	176	2
C ₁ '-C ₂ '	1.40	0.04	Av FeCO	176	
Av C ₁ C ₂	1.44		$\angle CFeC^a$		
C ₁ -C ₁ '	1.48	0.04	C ₅ Fe'C ₁ '	94	1
C ₁ '-C ₁ '	1.50	0.04	C ₅ FeC ₁	96	1
Av C ₁ C ₁	1.49		C ₅ FeC ₁	93	1
			C ₅ FeC ₁ '	95	1
			Av	94	

Table 3 (cont'd.)

Fe'-C ₆ ¹	1.81	0.03	C ₆ FeC ₁	88	1
Fe'-C ₆ ¹	1.76	0.03	C ₆ ¹ FeC ₁ ¹	95	1
Fe'-C ₅ ¹	1.73	0.03	C ₆ ¹ Fe'C ₁ ¹	89	1
Fe-C ₅	1.77	0.03	C ₆ ¹ ¹ Fe'C ₁ ¹ ¹	90	1
Fe-C ₆	1.76	0.04	Av	91	
Fe-C ₆ ¹	1.77	0.02	C ₆ FeC ₆ ¹	91	1
Av FeC(CO)	1.77		C ₆ ¹ ¹ Fe'C ₆ ¹	94	1
CO(CO)			Av	93	
C ₆ ¹ ¹ -O ₆ ¹ ¹	1.13	0.03	C ₁ FeC ₁ ¹	82	1
C ₅ ¹ -O ₅ ¹	1.20	0.03	C ₁ ¹ FeC ₁ ¹ ¹	83	1
C ₆ ¹ -O ₆ ¹	1.13	0.03	Av	83	
C ₅ -O ₅	1.14	0.03	C ₅ FeC ₆	101	1
C ₆ -O ₆	1.16	0.04	C ₅ FeC ₆ ¹	102	1
C ₆ ¹ -O ₆ ¹	1.15	0.03	C ₅ ¹ Fe'C ₆ ¹ ¹	97	1
Av CO	1.15		C ₅ ¹ Fe'C ₆ ¹	101	2
			Av	100	

2p π , 2p π ^b	Angle	σ^- Av.	Si _j ^c
C ₂ , C ₂ ¹ type: C ₂ ¹ , C ₂ ¹ ¹	3	4	0.34
C ₂ , C ₂ ¹	4	5	
C ₁ , C ₁ ¹ type: C ₁ ¹ , C ₁ ¹	95	4	0.04
C ₁ ¹ ¹ , C ₁ ¹ ¹	101	4	
C ₁ , C ₂ type: C ₁ ¹ ¹ , C ₂ ¹ ¹	60	4	0.16
C ₂ , C ₁ ¹	57	4	
C ₁ , C ₂	68	4	
C ₁ ¹ ¹ , C ₂ ¹ ¹	59	5	

a. Test of octahedral (90°) bonding about Fe, Fe to C₂--C₂¹ π orbital omitted.

b. The 2p π orbital for C₁ is taken as perpendicular to the plane of C_jC₁C_k, where C_j and C_k are bonded to C₁.

c. Overlap integrals Si_j are discussed later in the text.

Table 4. Atomic Parameters^a and Standard Deviations (σ)
for (COT)Fe(CO)₃

Atom	x ₁	y ₁	z ₁	x ₁	y ₁	z ₁
Fe	0.7690	-0.0613	0.7500	0.0003	0.0002	-----
C ₅	.504	-.097	.750	.002	.001	-----
O ₅	.335	-.110	.750	.002	.001	-----
C ₆	.867	-.140	.637	.002	.001	0.001
O ₆	.930	-.192	.568	.002	.001	.001
C ₂	.917	.062	.688	.001	.001	.001
C ₁	.739	.054	.618	.002	.001	.001
C ₃	.558	.115	.608	.002	.001	.001
C ₄	.442	.164	.685	.002	.001	.001

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0074	0.0022	0.0033	-0.0000	0	0
C ₅	.013	.002	.012	-.002	0	0
O ₅	.013	.008	.018	-.004	0	0
C ₆	.016	.004	.005	.001	-.000	.001
O ₆	.042	.006	.008	.004	-.005	.002
C ₂	.018	.005	.007	.002	.002	.001
C ₁	.020	.004	.005	-.002	-.000	.001
C ₃	.020	.003	.009	-.001	-.004	.002
C ₄	.016	.003	.011	-.000	-.005	.001

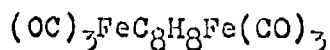
^a The other half of the molecule is generated by a mirror plane at $z = 3/4$.

Table 5. Distances (in Å), Angles ($^{\circ}$) and Standard Deviations (σ) for (COT)Fe(CO)₃

FeC(COT)	Dist.	σ	CCC	Angle	σ	
Fe-C ₂	2.05	0.01	C ₁ C ₂ C ₂ '	124.6	0.5	
Fe-C ₁	2.18	0.01	C ₂ C ₁ C ₃	132.4	1.0	
C(COT)C(COT)			C ₂ C ₃ C ₄	133.2	1.2	
C ₂ -C ₂ '	1.42	0.02	C ₂ C ₃ C ₄ '	131.8	0.7	
C ₂ -C ₁	1.42	0.01	FeCO			
C ₁ -C ₃	1.45	0.02	FeC ₅ O ₅	172.9	1.5	
C ₃ -C ₄	1.34	0.02	FeC ₆ O ₆	178.2	1.0	
C ₄ -C ₄ '	1.49	0.03	CFeC ^a			
C ₁ -C ₁ '	3.04	0.02	C ₁ FeC ₁ '	88.5	0.5	
C ₃ -C ₃ '	3.27	0.03	C ₅ FeC ₁	96.0	0.4	
C ₂ -C ₄	3.34	0.02	C ₅ FeC ₁	87.0	0.4	
FeC(CO)	.		C ₆ FeC ₁ '	92.7	0.7	
Fe-C ₆	1.79	0.01	C ₆ FeC ₅	100.7	0.5	
Fe-C ₅	1.80	0.02	C ₆ FeC ₁ '	163.0	0.5	
CO(CO)			2p π , 2p π ^b			S _{1,j} ^c
C ₅ -O ₅	1.12	0.02	C ₂ C ₂ '	0	0	0.33
C ₆ -O ₆	1.13	0.01	C ₂ -C ₁	60.2	1.3	.16
			C ₁ -C ₃	39.2	1.9	.25
			C ₃ -C ₄	8.8	1.7	.30
			C ₄ -C ₄ '	0	0	.31

a,b,c See corresponding footnotes to Table 3.

Table 6. Observed Structure Factors^a for



$h = 0$ (k, l): (0,2-10) 126,a,82,a,20,a,17,a,21;
 (1,1-9) 36,10,43,29,47,a,39,a,16; (2,3-9) 12,14,
 17,17,18,18,16; (3,1-10) 37,10,11,34,28,30,a,
 22,a,10; (4,0-9) 20,164,44,101,23,14,a,a,12,17;
 (5,1-10) 21,a,40,34,27,a,a,22,a,14; (6,4-9) 10,
 24,a,10,12,12; (7,1-10) 34,a,19,a,39,a,22,a,a,18;
 (8,0-8) 177,a,86,48,40,26,a,a,11; (9,2-9) 25,16,
 22,a,20,22,a,10; (10,6-8) 14,a,12; (11,1-8) 10,
 18,16,18,a,21,a,11; (12,0-8) 18,64,20,41,14,a,a,
 a,18; (13,3-7) 14,12,14,a,12; (14,5) 10; (15,5)
 14; (16,0-4) 24,a,20,10,14; (18,1) 30.
 $h = -1$ (k, l): (0,3-9) 14,a,33,a,40,a,22; (1,2-8)
 18,52,a,64,a,50,21; (2,1-8) 185,149,a,a,24,23,a,
 18; (3,1-8) 17,31,a,37,21,35,a,18; (4,6) 23;
 (5,3-7) 18,33,23,28,18; (6,1-5) 55,98,a,67,20;
 (7,1-7) 20,27,27,a,46,a,26; (8,7) 20; (9,3-8)
 33,25,18,a,27,18; (10,1-5) 77,a,55,a,33; (11,3)
 22; (13,3-6) 24,a,a,22; (14,2-4) 51,a,21; (17,6)
 7; (18,1-3) 28,a,16.
 $h = 1$ (k, l): (0,1-7) 16,a,18,a,27,a,31; (1,1-8)
 85,16,64,a,47,20,29,16; (2,0-9) 201,141,232,73,
 40,a,a,a,a,18; (3,0-9) 14,20,85,a,41,a,33,a,a,
 20; (4,1-8) 13,12,a,22,a,a,a,14; (5,0-5) 57,13,
 51,a,47,43; (6,0-8) 137,84,128,86,34,21,a,18,20;
 (7,1-7) 50,22,51,21,29,a,18; (8,3-7) 17,a,a,a,18;
 (9,1-6) 30,a,29,a,25,17; (10,0-5) 71,71,35,39,
 17,27; (11,2-6) 18,16,20,a,20; (13,4-5) 19,18;
 (14,0-2) 46,30,35; (18,1) 15.
 $h = -2$ (k, l): (0,2-10) 174,a,31,a,49,a,20,a,29;
 (1,1-9) 23,a,87,a,38,37,49,a,24; (2,3-8) 16,a,16,
 18,22,28; (3,1-10) 14,39,59,35,24,33,23,40,a,23;
 (4,1-7) 76,96,157,a,56,a,25; (5,3-10) 24,a,48,32,
 28,a,a,23; (7,2-7) 18,40,32,42,a,23; (8,1-6) 54,
 84,22,42,a,31; (9,3-7) 20,29,a,21,25; (11,2-6)
 21,a,20,a,25; (12,1-4) 55,46,38,22; (16,1-2) 21,
 23.
 $h = 2$ (k, l): (0,0-10) 280,a,141,a,102,a,12,a,22,
 a,14; (1,0-6) 37,80,51,60,86,64,20; (2,1-8) 14,
 18,21,20,29,25; (3,0-6) 11,51,85,30,42,23,22;
 (4,0-9) 81,223,28,56,21,17,a,23,a,23; (5,0-8)
 48,40,53,55,61,31,a,a,22; (6,2-7) 22,18,a,20,
 a,18; (7,1-8) 51,72,58,a,33,a,21,17; (8,0-6)
 100,a,75,25,49,a,18; (9,1-5) 29,23,a,a,26;
 (11,0-4) 21,a,22,a,22; (12,0-3) 43,50,a,22;
 (13,1-3) 21,a,21; (16,0) 25.

$h = -3(k, \ell)$: (0,5-9) 16,a,28,a,28; (1,1-10) 23,a,57,31,47,a,45,22,31,24; (2,1-7) 146,22,101,115,74,20,20; (3,2-8) 42,20,32,a,39,a,41; (4,6-8) 22,a,20; (5,1-8) 16,a,a,17,a,41,20,20; (6,1-6) 33,98,55,94,77,22; (7,1-7) 17,18,35,a,41,a,33; (9,3-7) 20,21,22,a,24; (10,1-5) 66,26,54,a,25; (11,6) 20; (13,2-6) 44,a,32,a,20; (14,2-4) 51,a,34; (18,1) 30.

$h = 3(k, \ell)$: (0,3-7) 41,a,43,a,17; (1,1-6) 32,21,a,a,60,25; (2,0-6) 95,a,21,33,51,a,21; (3,1-6) 18,82,26,69,a,32; (4,1-6) 27,a,41,a,20; (5,0-7) 44,24,74,33,58,26,20,17; (6,0-6) 109,28,84,43,a,18,21; (7,0-7) 18,39,17,59,a,31,22,18; (8,3-5) 18,a,23; (9,0-6) 17,37,21,29,a,29,23; (10,1-3) 40,a,26; (11,0-4) 18,26,a,a,28; (13,2) 24; (14,0-2) 53,a,24;

$h = -4(k, \ell)$: (0,2-6) 377,a,49,a,47; (1,1-9) 14,a,a,a,35,28,38,a,24; (2,8) 20; (3,1-8) 18,23,a,a,21,42,25,40; (4,1-7) 112,42,155,42,131,a,25; (5,2-8) 16,17,a,45,43,26,21; (7,1-7) 28,a,27,a,35,22,36; (8,2-6) 111,a,65,21,39; (9,5-6) 21,21; (12,1-5) 44,36,44,21,35; (16,2-4) 25,a,21.

$h = 4(k, \ell)$: (0,0-8) 42,a,71,a,26,a,20,a,30; (1,0-7) 14,22,29,54,21,52,a,24; (2,2-6) 16,20,28,25,27; (3,0-6) 20,a,52,21,56,a,40; (4,0-9) 85,93,16,a,16,a,a,a,a,17; (5,1-6) 44,47,44,30,37,37; (6,1-5) 29,a,32,a,20; (7,1-5) 41,22,47,a,30; (8,0-6) 52,a,39,a,a,a,21; (9,0-5) 27,18,22,a,a,34; (11,0-4) 29,25,27,a,27; (12,0-2) 46,27,17; (16,0) 22.

$h = -5(k, \ell)$: (0,1-9) 13,a,a,a,a,a,23,a,23; (1,1-9) 64,a,a,a,37,a,41,a,24; (2,1-7) 85,71,181,90,56,a,34; (3,1-8) 25,22,a,a,a,51,a,37; (5,2-8) 42,a,21,a,52,a,31; (6,1-7) 57,99,79,80,52,53,25; (7,1-7) 37,a,20,a,29,a,29; (9,1-7) 23,a,a,a,18,a,20; (10,1-7) 49,41,53,21,39,a,30; (14,2-4) 44,a,38.

$h = 5(k, \ell)$: (0,3-5) 23,a,36; (1,1-6) 35,a,36,23,37,28; (2,0-6) 96,31,12,17,20,a,26; (3,0-7) 55,a,29,a,33,a,a,21; (4,0-6) 10,a,a,a,18,a,29; (5,0-6) 42,18,42,43,17,a,22; (6,0-6) 103,64,30,a,a,a,25; (7,1-6) 37,24,33,a,29,20; (8,5) 23; (9,0) 30; (10,5) 21; (11,0) 13; (14,0) 46.

$h = -6(k, \ell)$: (0,2-8) 170,a,134,a,46,a,37; (1,1-8) 63,23,a,21,41,16,a,21; (3,1-8) 47,a,a,a,29,29,a,22; (4,1-7) 161,43,56,35,134,a,50; (4,1-7) 161,43,56,35,a,50; (5,2-8) 22,a,2,23,22,31,22; (7,1-7) 35,a,a,a,22,29,27; (8,2-6) 82,a,a,a,37,22,28; (9,1) 28; (12,1-7) 38,29,50,a,39,a,20.

$h = 6$ (k, ℓ): (0,0-8) 46,a,25,a,30,a,39,a,23;
 (1,0-5) 30,48,21,48,a,26; (2,0-4) 10,17,14,
 16,20; (3,0-6) 62,25,35,a,33,a,21; (4,0-1)
 12,21; (5,0-6) 30,35,30,28,25,a,30; (7,0-3)
 42,42,a,20; (8,0-6) 50,a,20,a,22,a,20; (9,0-3)
 31,a,a,21; (11,0-2) 24,a,22; (12,0) 26; (16,0)
 16; (6,3) 20.
 $h = -7$ (k, ℓ): (0,1) 11; (1,1-5) 52,a,a,a,22;
 (2,1-8) 29,105,122,67,79,84,38,23; (3,8) 17;
 (6,1-7) 49,77,33,a,39,52,31; (7,1-2) 35,22;
 (9,1) 34; (10,1-7) 36,23,40,a,51,a,32; (14,2-6)
 35,a,27,a,21.
 $h = 7$ (k, ℓ): (0,1-5) 31,a,33,a,14; (1,1-4) 65,
 a,46,26; (2,0-4) 18,15,a,30,32; (3,0-2) 59,24,
 37; (4,0-2) 17,a,21; (5,0-3) 51,19,31,20;
 (6,0-1) 66,21; (7,1-5) 37,a,22,a,21; (9,0) 21;
 (11,0-2) 18,a,20; (13,0) 22; (14,0) 20.
 $h = -8$ (k, ℓ): (0,2-8) 67,a,182,a,38,a,30;
 (1,1-3) 35,23,18; (3,4) 18; (4,1-7) 79,18,
 64,a,64,a,55; (5,1-7) 28,a,a,a,a,a,21; (7,1-3)
 34,a,20; (8,2-8) 53,a,69,22,35,29,25; (9,2)
 26; (11,2) 26; (12,1-7) 31,a,35,a,a,a,31.
 $h = 8$ (k, ℓ): (0,0-6) 78,a,22,a,25,a,28;
 (1,0-3) 31,53,25,43; (2,0-1) 14,20; (3,0-4)
 39,27,39,a,22; (4,0) 26; (5,0-4) 37,25,a,a,16;
 (7,0-1) 12,36; (8,0-4) 38,a,a,a,a,69; (9,0) 23;
 (11,0-2) 23,a,18; (13,0) 15.
 $h = -9$ (k, ℓ): (0,1) 12; (1,1-9) 34,a,39,a,a,
 a,a,a,25; (2,1-9) 29,70,37,41,58,37,29,23,18;
 (3,2-10) 39,a,28,a,a,a,25,a,20; (5,2-8) 29,a,
 a,a,a,a,24; (6,1-8) 44,54,a,48,a,39,a,22;
 (7,1-3) 35,a,21; (9,1-9) 21,31,25,a,a,a,a,a,21;
 (10,3-9) 34,a,a,a,28,a,16.
 $h = 9$ (k, ℓ): (0,1-3) 29,a,32; (1,1-3) 43,a,33;
 (2,0) 29; (3,0-2) 41,a,30; (4,0) 17; (5,0-1)
 37,24; (6,0-1) 22,21; (7,0-1) 14,30; (9,0-1)
 13,23; (10,0) 15; (11,0) 23; (13,0) 19.
 $h = -10$ (k, ℓ): (0,2-10) 20,a,60,a,59,a,30,a,
 22; (1,1-3) 29,18,31; (3,2) 40; (4,3-9) 40,
 a,a,a,70,a,32; (5,1-2) 22,26; (7,1-3) 38,23,
 22; (8,5-8) 25,a,a,22; (9,2-3) 21,27; (12,5)
 24.
 $h = 10$ (k, ℓ): (0,0-6) 42,a,a,a,25,a,16;
 (1,0-3) 29,41,a,24; (2,0) 12; (3,0-2) 26,a,25;
 (4,3-5) 25,a,23; (5,0) 29; (7,1-5) 23,a,a,a,
 16; (8,0) 18; (9,0-1) 14,23; (11,0) 21; (13,0)
 12.
 $h = -11$ (k, ℓ): (1,1-3) 26,a,23; (2,4-10) 31,
 46,39,47,25,25,20; (3,2) 36; (5,1-2) 22,34;
 (6,2) 23; (7,1-3) 26,a,23.

$h = 11$ (k, ℓ): (0,1-3) 23,a,14; (1,1) 39;
 (3,0) 27; (4,0) 17; (5,0) 22; (11,0) 17.
 $h = -12$ (k, ℓ): (0,4-8) 26,a,77,a,20; (1,1)
 22; (3,2) 30; (4,1-9) 23,a,29,44,a,47,a,
 42; (5,2) 22; (7,1) 24; (8,4-8) 26,a,39,
 a,22.
 $h = 12$ (k, ℓ): (0,0-4) 16,a,a,a,16; (1,1) 28;
 (3,0) 23; (4,0) 12; (11,0) 13.
 $h = -13$ (k, ℓ): (2,4-7) 25,32,24,35; (3,2)
 24; (5,2) 28.
 $h = 13$ (k, ℓ): (1,0) 14; (9,0) 10.
 $h = -14$ (k, ℓ): (0,4-8) 14,a,27,a,21; (3,2)
 23; (4,9) 35.
 $h = 14$ (k, ℓ): (0,0-2) 16,a,18; (2,0) 17;
 (3,0) 17.

^a Range of ℓ and value of k are indicated
 in parentheses. Absences are indicated
 by the symbol, a.

Table 7. Observed Structure Factors^a for $C_8H_8Fe(CO)_3$.

$l = 0$ (h,k): (2-6,0) 23,47,42; (2-8,1) 58,38,16,a,a,22,14; (0-8,2) 79,54,99,21,53,25,26,12,11; (1-8,3) 29,31,12,45,13,25,14,8; (0-7,4) 91,16,40,92,14,14,a,14; (1-7,5) 50,25,20,27,a,34,8; (0-6,6) 52,41,55,21,36,25,15; (1-7,7) 36,17,a,17,a,a,25; (0-6,8) 85,16,49,18,44,a,34; (1-7,9) 30,a,14,a,15,11,11; (0-6,10) 45,31,46,14,23,24,23; (1-4,11) 14,18,8,32; (0-5,12) 12,33,13,29,a,9; (2-6,13) 13,8,11,a,10; (0-3,14) 16,12,23,20; (1,15) 22; (0-2,16) 27,a,22.

$l = 1$ (h,k): (2-8,0) 85,a,18,a,21,a,19; (1-8,1) 117,48,50,6,51,a,29,15; (1-8,2) 43,a,9,25,11,14,21,16; (0-8,3) 53,53,84,34,41,28,a,a,18; (1-9,4) 67,31,32,13,32,a,18,a,15; (0-7,5) 35,29,43,a,53,24,23,11; (1-8,6) 9,a,23,26,30,a,12,15; (0-7,7) 9,66,21,36,16,42,12,17; (1-8,8) 24,25,a,5,11,26,a,17; (0-7,9) 20,59,a,49,25,18,a,17; (2-8,10) 22,12,a,16,a,a,11; (0-5,11) 17,32,38,17,25,15; (3-5,12) 20,a,21; (0-6,13) 27,9,30,14,15,a,13; (2-5,14) 14,a,a,14; (1-5,15) 32,15,a,a,18; (0-3,17) 9,22,a,18.

$l = 2$ (h,k): (0-8,0) 101,a,68,a,48,a,25,a,12; (1-7,1) 6,22,23,41,11,a,24; (0-8,2) 91,45,44,54,34,37,22,14,12; (1-9,3) 60,25,5,41,a,20,14,8,20; (0-7,4) 45,61,a,71,6,35,a,16; (1-8,5) 25,10,a,17,13,30,16,13; (0-7,6) 71,40,38,61,30,16,11,13; (1-7,7) 11,19,17,15,12,a,18; (0-6,8) 57,18,45,a,35,13,25; (1-5,9) 6,7,21,11,18; (0-6,10) 47,29,26,26,17,14,23; (1-6,11) 19,a,a,16,6,11; (1-5,12) 37,12,31,a,16; (6,13) 10; (0-3,14) 19,18,16,24; (1,15) 10; (0-2,16) 18,a,22.

$l = 3$ (h,k): (2-8,0) 32,a,28,a,31,a,19; (0-8,1) 15,23,56,62,34,29,a,18,15; (1-8,2) 77,46,15,10,19,19,16,11; (0-8,3) 121,57,63,27,58,19,20,a,13; (1-7,4) 10,24,22,8,20,a,17; (0-8,5) 92,19,81,a,44,21,25,a,15; (1-6,6) 13,32,21,11,20,14; (0-7,7) 25,50,57,30,19,22,12,12; (1-8,8) 23,a,a,23,12,12,a,14; (0-5,9) 7,47,20,25,11,19; (1-6,10) 5,a,12,a,12,14; (0-6,11) 26,12,41,a,26,12,14; (1-5,12) 13,a,a,a,17; (0-6,13) 28,15,36,a,24,13,16; (1-5,14) 9,a,a,a,13; (0-5,15) 20,19,17,14,a,13; (1-3,17) 16,a,11.

$\ell = 4$ (h,k): (0-8,0) 23,a,64,a,46,a,13,a,10; (1-7,1) 5,16,11,23,20,a,28; (0-7,2) 54,46,32,54,28,48,11,15; (1-8,3) 19,a,27,32,a,13,a,8; (0-7,4) 16,82,5,62,7,41,a,20; (2-8,5) 27,a,17,a,12,17,10; (0-7,6) 52,68,29,52,23,14,a,17; (3-7,7) 34,a,15,a,11; (0-6,8) 50,a,30,12,23,13,16; (2-5,9) 11,20,8,20; (0-6,10) 16,35,19,24,20,5,14; (5-6,11) 12,14; (0-5,12) 14,34,a,40,a,22; (6,13) 13; (0-5,14) 11,27,15,22,18,17; (0-2,16) 13,10,20; (1,17) 9; (1,18) 8.
 $\ell = 5$ (h,k): (2-8,0) 24,a,21,a,31,a,14; (0-7,1) 68,42,a,46,25,34,27,12; (1-7,2) 16,6,a,26,a,15,18; (0-8,3) 77,30,59,28,49,8,19,a,8; (2-5,4) 11,24,a,16; (0-8,5) 70,a,65,31,29,23,23,a,27; (1-6,6) 59,13,18,21,a,11; (0-7,7) 34,51,20,27,14,16,16,10; (2-5,8) 18,a,14,14; (0-5,9) 38,37,10,25,a,20; (1-6,10) 14,10,a,17,a,15; (0-6,11) 29,a,31,21,23,18; (5,12) 18; (0-6,13) 22,a,32,a,17,a,21; (1,14) 8; (0-1,15) 20,15; (1,17) 12.
 $\ell = 6$ (h,k): (0-6,0) 78,a,57,a,53,a,10; (1-7,1) 14,31,9,a,19,15,14; (0-7,2) 38,31,54,35,37,24,11,11; (1-8,3) 17,20,22,17,a,18,a,8; (1-5,4) 52,a,43,a,29; (1-5,5) 35,18,9,21,8; (0-7,6) 50,52,31,9,27,20,10,9; (2-7,7) 9,21,a,14,10,10; (0-5,8) 44,a,41,a,31,11; (1-5,9) 13,12,a,a,15; (1-5,10) 29,40,a,23,12; (5-6,11) 9,10; (0-5,12) 12,28,a,a,a,18; (6,13) 7; (1-2,14) 19,16; (0-2,16) 24,a,17.
 $\ell = 7$ (h,k): (2-6,0) 11,a,40,a,12; (0-7,1) 34,56,11,49,12,35,a,9; (3-7,2) 13,14,a,10,13; (0-8,3) 54,25,33,34,23,a,11,a,8; (1-4,4) 24,a,20,14; (0-6,5) 40,18,30,11,26,12,23; (1-6,6) 24,a,11,a,12,10; (0-6,7) 24,38,a,46,11,18,14; (4-6,8) 11,11,13; (0-5,9) 16,35,a,a,a,18; (4,10) 12; (0-6,11) 34,20,14,a,a,a,19; (1-5,12) 9,a,a,a,13; (0-2,13) 20,a,18; (1,14) 14.
 $\ell = 8$ (h,k): (0-4,0) 56,a,68,a,44; (1-5,1) 16,14,17,a,10; (0-7,2) 52,25,36,26,31,a,13,11; (2-6,3) 34,a,a,14; (0-5,4) 19,43,5,9,a,31; (3-6,5) 10,13,a,14; (0-6,6) 44,23,20,17,31,a,10; (0-6,8) 17,a,50,a,33,11,17; (1-5,9) 9,a,a,a,15; (0-5,10) 24,18,35,a,15,12; (2,11) 13; (0-5,12) 12,28,a,a,a,15; (1-2,13) 7,14; (0-2,14) 12,11,15; (2,16) 18.

$\ell = 9$ (h,k): (4,0) 28; (0-7,1) 24,42,15,38,a,17,a,8;
 (2-6,2) 10,16,8,a,9; (0-6,3) 55,14,24,23,15,a,12;
 (1-2,4) 17,9; (0-4,5) 26,14,26,10,26; (3-6,6) 8,7,a,12;
 (0-3,7) 8,a,15,39; (2-5,8) 9,a,15,13; (1-5,9) 32,a,22,10,16;
 (0-2,11) 27,16,14; (1,12) 15; (0-2,13) 18,a,26;
 (1,15) 14; (1,17) 13.
 $\ell = 10$ (h,k): (0-4,0) 38,a,36,a,21; (2-7,1) 10,13,a,a,a,10;
 (0-5,2) 20,34,25,10,17,15; (1-2,3) 8,9; (1-3,4) 37,a,27;
 (3,5) 8; (0-4,6) 13,23,21,22,20; (2,7) 11; (0-4,8) 22,a,26,a,18;
 (5,9) 11; (0-4,10) 17,14,14,12,11; (2,11) 13; (1,12) 24;
 (1,14) 13.
 $\ell = 11$ (h,k): (2-4,0) 14,a,10; (0-7,1) 29,20,a,17,a,a,a,8;
 (4,2) 11; (0-6,3) 37,a,26,11,21,a,8; (0-4,5) 29,a,32,15,26;
 (1,6) 14; (0-3,7) 14,a,15,15; (4,8) 11; (0-5,9) 11,18,a,a,a,11;
 (0-2,11) 14,a,20; (2,13) 18; (1,15) 13.
 $\ell = 12$ (h,k): (0-4,0) 21,a,18,a,17; (0-5,2) 14,21,16,16,a,13;
 (1-3,3) 9,a,8; (1-3,4) 33,a,27; (2,5) 9; (0-3,6) 16,26,11,16;
 (3,7) 9; (0-2,8) 20,a,12; (1-2,10) 13,9; (1,12) 16; (1,14) 17.
 $\ell = 13$ (h,k): (4,0) 9; (1-3,1) 18,11,11; (0-4,3) 17,13,21,a,13;
 (0-2,5) 27,8,20; (3,7) 12; (1,9) 14.
 $\ell = 14$ (h,k): (0-2,0) 22,a,21; (0-2,2) 20,7,14; (1,3) 8;
 (1-3,4) 17,a,14; (0-2,6) 19,13,12; (3,7) 8; (2,8) 20;
 (1,10) 11.
 $\ell = 15$ (h,k): (1,1) 22; (1-2,3) 6,13; (2,5) 13; (1,7) 16;
 (1,9) 16.

^a Range of h and value of k are indicated in parentheses, and an absence is indicated by a.

Table 8. Orbital overlaps in the Fe-butadiene
unit in $C_8H_8Fe(CO)_3$
2p carbon orbitals

Fe orbitals	C_1''	$C_1+C_1''^b$	$C_1-C_1''^a$	C_2	$C_2+C_2''^b$	$C_2-C_2''^a$
4s	.170	.236	0	.222	.272	0
$4p_x^c$	-.063	.042	-.144	.132	.094	.096
$4p_y$.129	.042	.144	.020	.094	-.096
$4p_z$	-.098	-.136	0	.096	.118	0
$3d_{z^2}$	-.028	-.040	0	.040	.050	0
$3d_{x^2-y^2}$.045	0	.066	-.024	0	-.042
$3d_{xy}$	-.024	-.034	0	-.008	-.009	0
$3d_{xz}$.004	.006	-.001	.004	-.036	.057
$3d_{yz}$.004	.006	.001	-.062	-.036	-.057
$(d^2sp^3)_z^d$	-.016	-.024	0	.182	.223	0
$(d^2sp^3)_{-z}$.122	.170	0	.046	.208	0
$(d^2sp^3)_x$.052	.138	-.068	.160	.126	.048
$(d^2sp^3)_{-x}$.150	.078	.134	-.026	.030	-.089
$(d^2sp^3)_y$.146	.138	.068	.106	.126	-.048
$(d^2sp^3)_{-y}$	-.036	.078	-.134	.076	.030	.089

a. Normalised antibonding orbital formed from indicated 2p orbitals.

b. Normalised bonding orbital formed as indicated.

c. All orbital subscripts refer to the axes on Fe in Fig. 3.

d. The octahedral hybrid orbitals of Fe are designated by (d^2sp^3) .

Legends for Figures

Figure 1. Side view of the $(OC)_3Fe(COT)Fe(CO)_3$ molecule, showing the nearly planar $C_1C_2C_2''C_1''$ group associated with Fe, and the $C_1'C_2'C_2'''C_1'''$ group coordinated to Fe'.

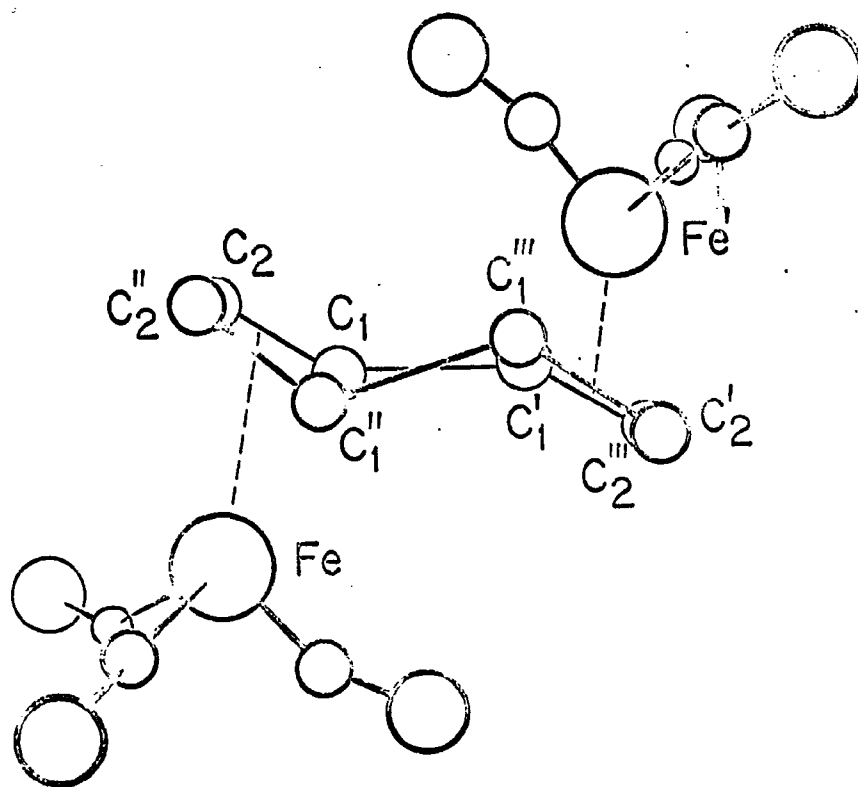
Figure 2. Projection of one $(OC)_3Fe(COT)Fe(CO)_3$ molecule along the a axis of half of the unit cell. The origin is at a center of symmetry. Other molecules have been omitted for clarity.

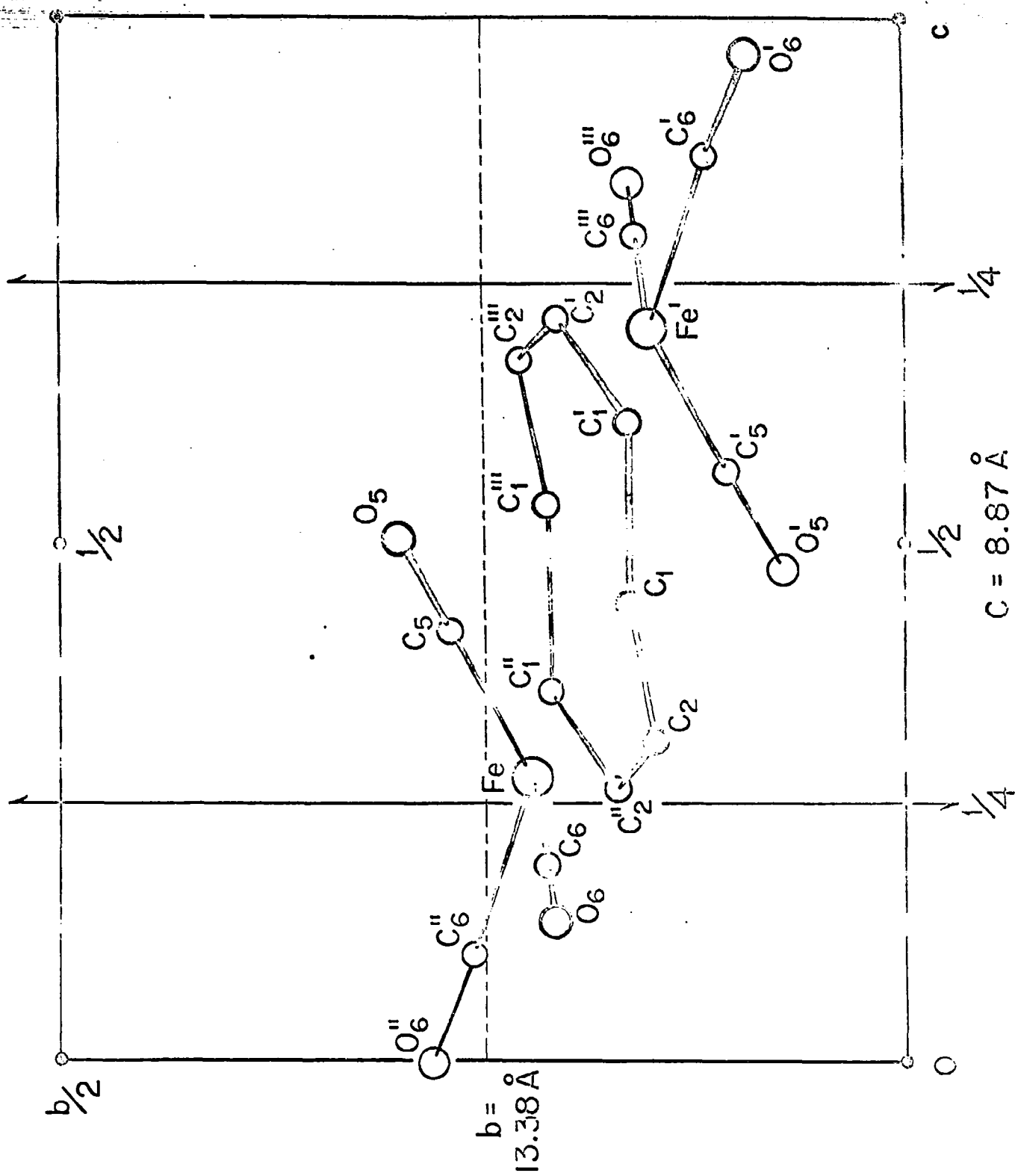
Figure 3. Side view of the $(COT)Fe(CO)_3$ molecule, projected along the c axis, with symmetry elements added according to the coordinates of the full circles. The open circles are added for perspective only. The COT ring forms two planes, the normals of which are 41° apart. Octahedral d^2sp^3 orbitals from Fe to CO are approximately indicated by lines, and from Fe to C_1 and C_1'' by O's; the remaining octahedral orbital, z , is hybridized with the three T_{2g} 3d orbitals to make ϕ and ϕ'' , which overlap, respectively, with the π orbitals from C_2 and C_2'' . The Fe orbitals in Table 8 are referred to the x, y and z axes shown.

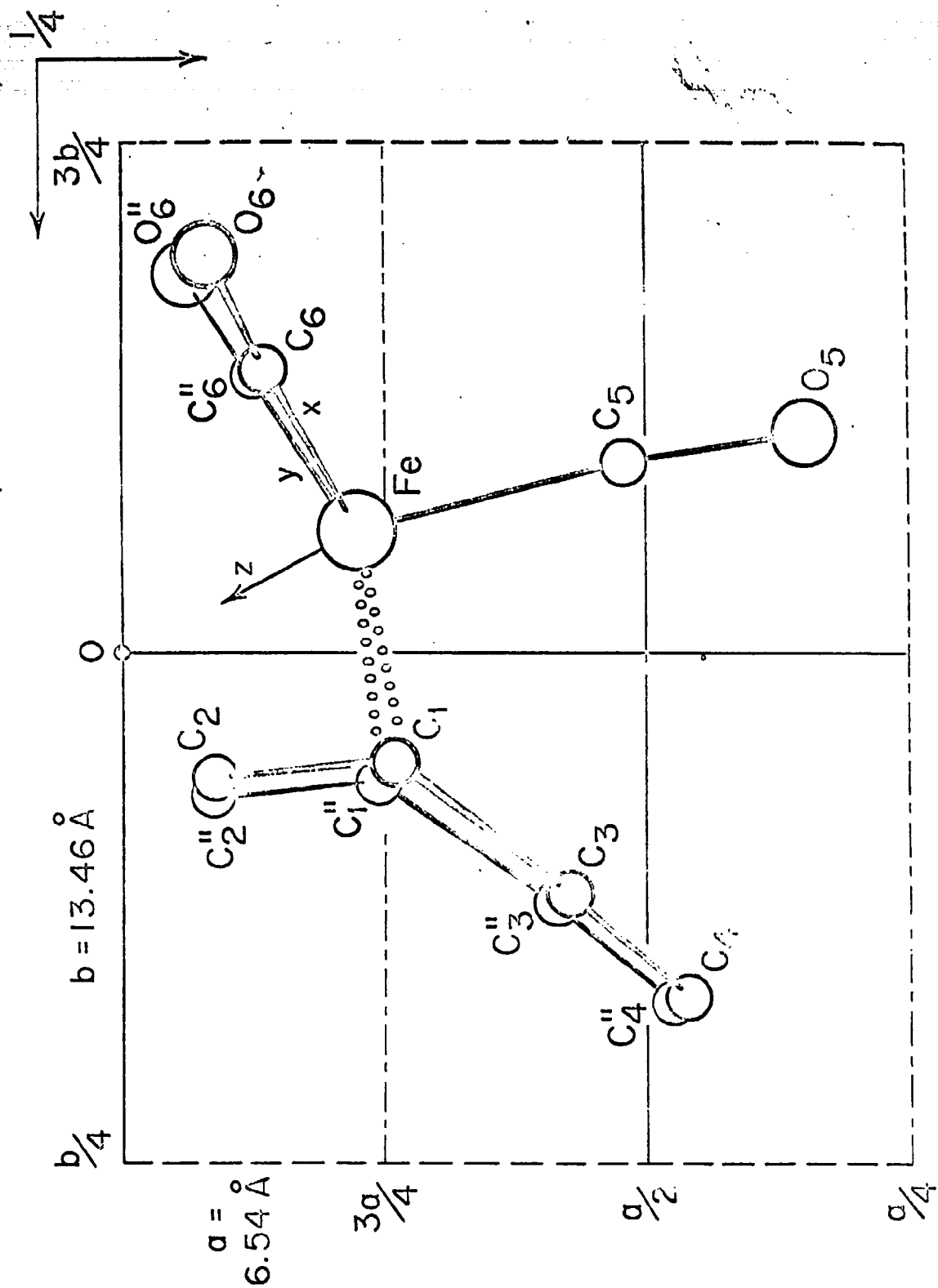
Figure 4. Back donation from filled d orbital of Fe to vacant antibonding π orbital of CO.

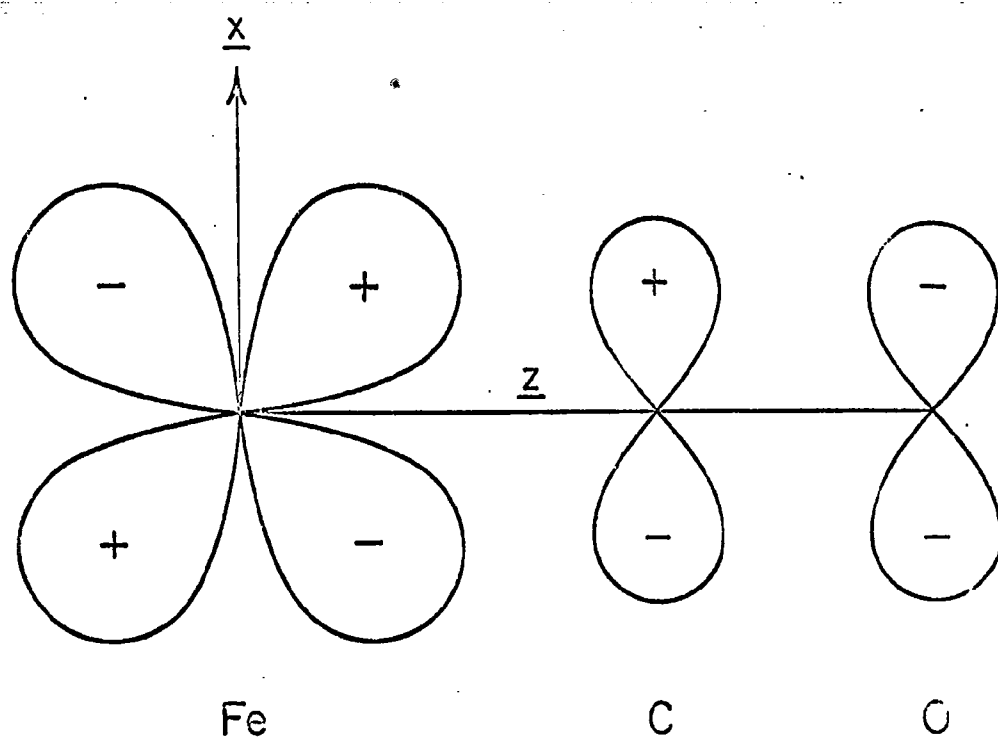
Figure 5. Projection of the dihedral form of the COT ring onto a planar octagon, shown as open circles 1.40 Å apart. The C₁, C₂, C₂^{''} and C₁^{''} atoms are bound to Fe in (COT)Fe(CO)₃.

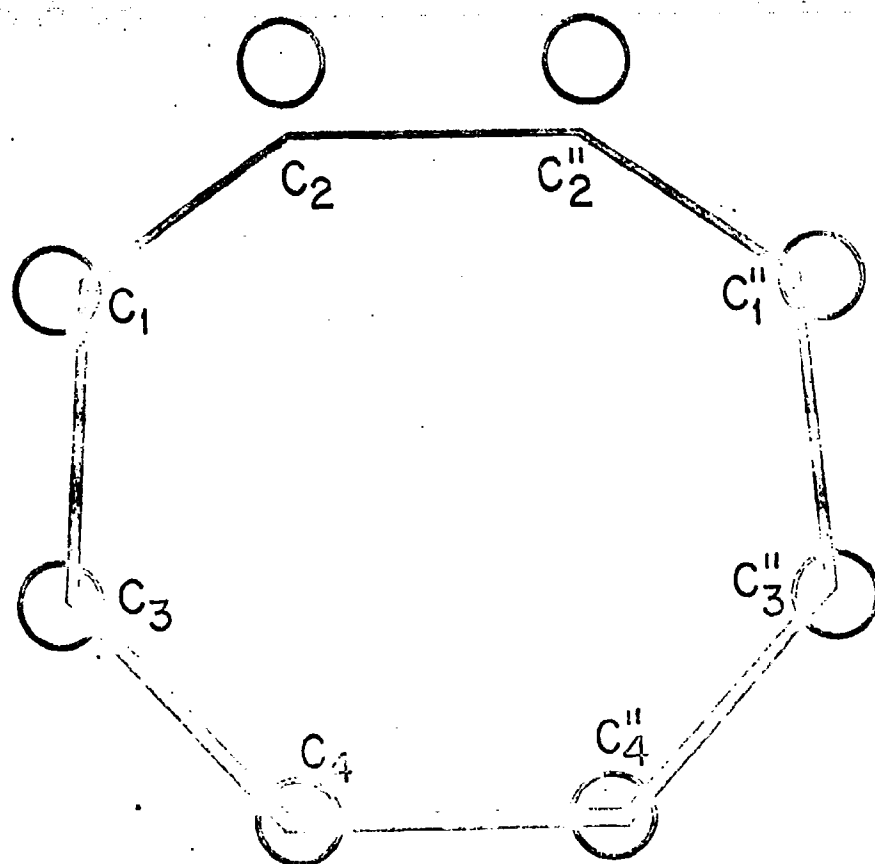
Figure 6. Molecular structures I²³, II²⁴, III²⁵, IV²⁶ in which the butadiene-iron residue has been observed by X-ray diffraction.

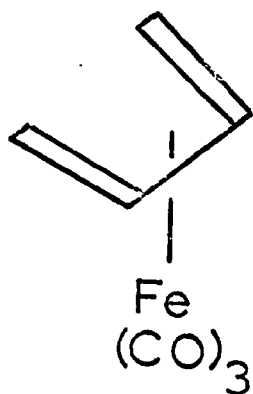




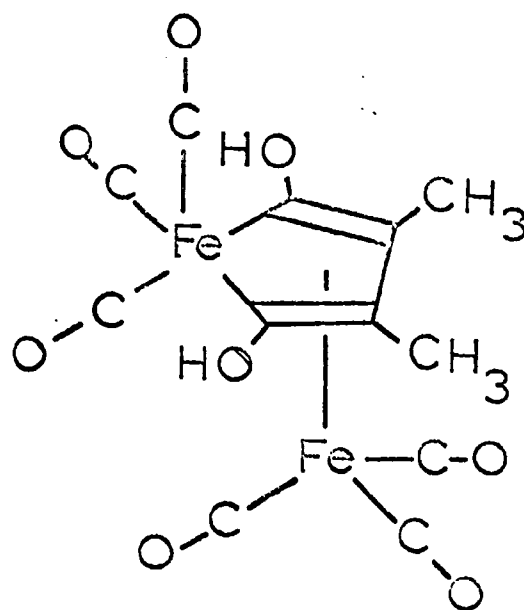




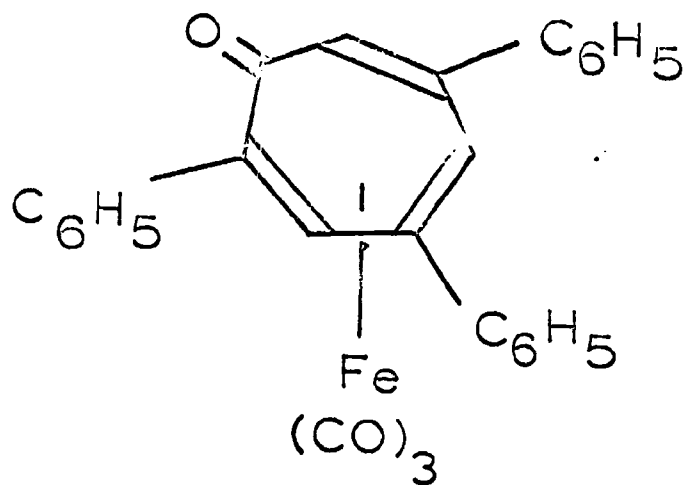




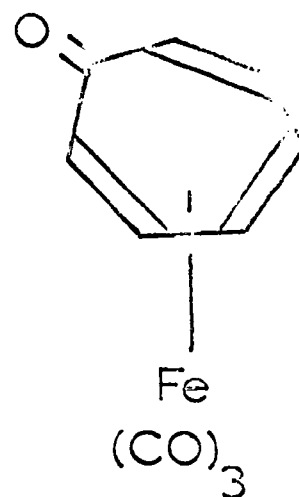
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